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Infrared spectra of some ternary organic conductors based on benzidine as a donor

Ashok N Patel, Parimal Trivedi and A T Oza*

Department of Physics, Sardar Patel University
Vallabh Vidyanagar-388 120, Gujarat, India

E-mail : ajayozat@yahoo.com

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Abstract The ternary organic charge transfer (CT) complexes namely benzidine-chloranil-I_2, benzidine-DDQ-I_2, benzidine-TCNQ-I and benzidine -TCNE-I, have been studied with infrared spectroscopy. Three-band model (two conduction band and one valence band) is concluded on the basis of two absorption edges. The ternary CT complexes differ from heavily doped semiconductors and organic alloys. Neutral to ionic transition model may be employed. Free carrier absorption reveals scattering of charge carriers by mainly ionized impurities *i.e.* by I_3^- ions at disordered. Band tailing reveals disordered nature of materials. Nature of transitions based on absorption function also reveal weakly disordered materials.

Keywords Ternary CTCs, two band model, absorption edges, band tailing, free-carrier absorption

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1. Introduction

The effect of doping of TMTTF (tetra methyl tetra thia fulvalene) in the superconducting $(TMTSF)_4ClO_4$ which is selenium analog, was studied at very low temperatures as a ternary system, quite sometime ago [1]. Also the effect of interchain Coulomb interactions on the metal-insulator transition was studied in a series of ternary system based on alkyl-ammonium donors with TCNQ-iodine as anionic sub-lattices [2]. Also substituted pyrene-TCNQ-ferrocene systems and substituted anthraquinone systems were studied [3,4]. A few more electrically conducting ternary compounds were also reported [5,6]. $(TMPD)_{1.5}$-KI-I_2 and $(TMPD)_{1.5}$-HI-I_2 can also be considered as ternary systems [7].

There are two types of ternary systems containing one donor and two acceptors and containing one acceptor and two donors. Among the first type, k-(BEDT-TTF)$_2$Cu[N(CN)$_2$Br] [8-11], k-(BEDT-TTF)$_2$Cu[N(CN)$_2$Y (Y=Cl, Br) [12,13], k-(BEDT-TTF)$_2$Cu[N(CN)$_2$]I [14] and $(C_1TET\text{-}TTF)(FeBr_4)_{1-x}(FeCl_4)_x$ [15] are the examples, many of which were organic superconductors. Those having two donors and one acceptor include α-(BEDT-TTF)$_2$NH$_4$Hg(SCN)$_4$ [16-18], α-(BEDT-TTF)$_2$MHg(SCN)$_4$ M=K, NH$_4$ [19-21], α-(BEDT-TTF)$_2$RbZn(SCN)$_4$ [22] and β-$(CH_3)_4$-As[Pd(dmit)$_2$] [23], some of which were also superconducting at low temperatures. Theories of unconventional density waves are also developed for interpreting electrical and optical properties [24-26].

Here, we report the infrared spectroscopic studies of benzidine-chloranil-iodine, benzidine-DDQ-iodine, benzidine-TCNQ-iodine and benzidine-TCNE-iodine having one donor and two acceptors in these 1:1:1 ternary conductors.

2. Experimental details

Benzidine-chloranil-I_2 in 1:1:1 molecular proportion was prepared as a ternary charge transfer complex by grinding the three molecular compounds in agate mortar with agate pastle for a long time. The complex was having dark blue colour as compared to green benzidine-chloranil binary complexes [27] and blue benzidine-I_2 binary complex [28]. The ternary complex was thus having deeper colour than the binary sub-systems.

Benzidine-DDQ-I_2 was also similarly prepared in the form of a 1:1:1 ternary complex. This complex was having still deeper

* Corresponding Author

indigo colour compared to the chloranil ternary complex because of DDQ having negative polarographic potential of half wave reduction similar to TCNQ and therefore, stronger CT interaction than chloranil

Benzidine-TCNQ-I_2 was also prepared because of strong CT interaction of TCNQ even compared to DDQ. Benzidine-TCNQ was studied earlier [29] It was semiconductor having less conductivity than benzidine-DDQ It is necessary to study the interplay of iodine charge transfer in this famous binary CT complex

Finally, benzidine-TCNE-I_2 was also prepared Benzidine interacts more strongly with TCNE than TCNQ In this case, it should be compared with pyridine-TCNE which is an exceptionally highly conducting, compared to all other TCNE salts [30] The amount of disorder is very less due to strong CT interaction

The infrared spectra of the ternary organic semiconductors in the form of almost transmitting pellets with spectrograde KBr were recorded using Perkin-Eslmer IR Spectrophotometer in the full mid-IR range, *i e* between 400 cm^{-1} and 4000cm^{-1}

3. Results and discussion

The infrared spectra of the four ternary charge transfer complexes are shown in Figure 1(a–d) The total range covered in 400 to 4000 cm^{-1} can be divided into mainly six parts in each of the four cases

The range above 3500 cm^{-1} corresponding to an absorption peak with a lot of noise can also be attributed to a free-carrier absorption [31,32] The noise can be associated with disordered positions of I_2 molecules and I_3 ions along the iodine sublattice

The second range 3000-3500 cm^{-1} mainly consists of the few bands forming a broad background envelope mainly due to the anions including bands due to water and hydrogen bonding The bands at 3453 cm^{-1}, 3340 cm^{-1}, 3280 cm^{-1} and 3160 cm^{-1} in benzidine-chloranil-I_2 and nearly at the same values in the other three ternary systems can be assigned to the high-frequency intramolecular vibrations of the organic acceptor molecules

All the bands in the 300-3500 cm^{-1} range of benzidine-TCNQ-I_2 complex (Figure 1c) are red-shifted to lower wavenumber side compared to those in the other complexes because of stronger electron – intramolecular vibration interaction (coupling) in TCNQ complex as explained with Rice's model [33] TCNQ complex is more radial-ion salt than other dative charge transfer complexes Free carrier density is more because of more charge transfer If electron –phonon coupling is strong, there will be red-shifts of the bands and anharmonic interactions are strong, there will be blue shifts of the bands.

The third range 2200-3000 cm^{-1} contains the donor levels stabilized as in the case of extrinsic semiconductors in the gap region which are sharp bands The background absorption corresponds to the exponentially decaying band region of the absorption edge [34]

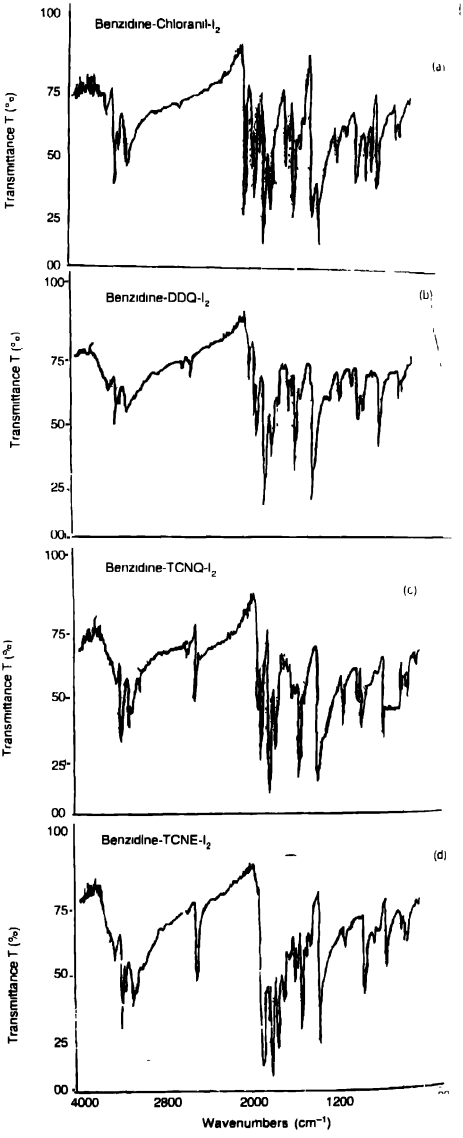

Figure 1. Infrared spectra of (a) Benzidine-Chloranil-I_2, (b) Benzidine-DDQ-I_2, (c) Benzidine-TCNQ-I_2 and (d) Benzidine-TCNE-I_2

The bands at nearly 2220 cm^{-1} in TCNE and TCNQ complexes are because of stretching vibration of C ≡ N bands This band is very weak in the spectrum of DDQ complex because of only two cyano groups and almost absent in the chloranil complex spectrum because of no cyano groups It can be clearly observed that the real part of refractive index (n^2–k^2) dominates in the transmission spectrum of TCNQ complex showing the dispersion shape In the TCNE complex, the imaginary part ($2nk$) dominates in the spectrum in the same range It is known within the Drude model, that n^2–k^2 is related to the imaginary part of conductivity and $2nk$ is related to the real part of optical conductivity [35]

The next range is at about 1700-2200 cm^{-1} range of absorption function corresponding to the nature of transition across the forbidden energy gap due to the Peierls transition This transition across the gap is always observed in a large number of cases of binary charge transfer complexes [14-24]

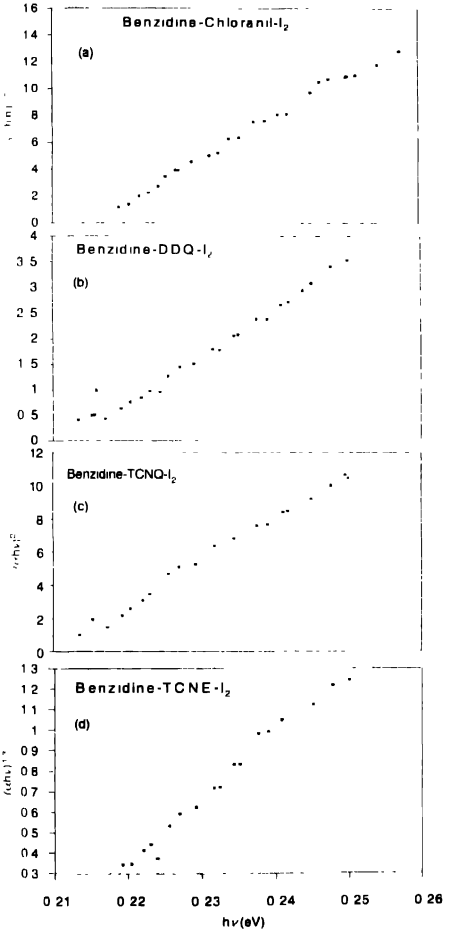

Figure 2. Infrared absorption edges of (a) Benzidine-Chloranil-I_2, (b) Benzidine-DDQ-I_2 , (c) Benzidine-TCNQ-I_2 and (d) Benzidine-TCNE-I_2

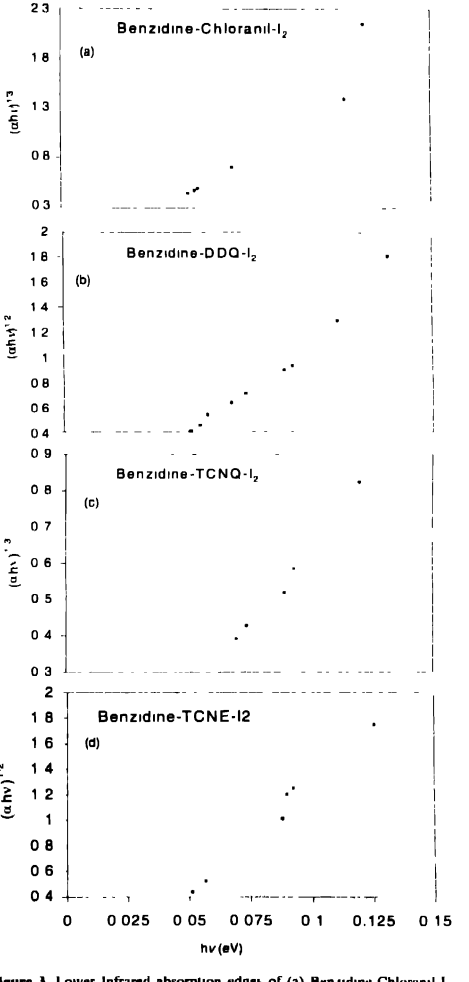

Figure 3. Lower Infrared absorption edges of (a) Benzidine-Chloranil-I_2, (b) Benzidine-DDQ-I_2 , (c) Benzidine-TCNQ-I_2 and (d) Benzidine-TCNE I_2

The fifth range between 1300-1700 cm^{-1} is an electronic absorption envelope considerably enhanced due to the coupling of electronic motions with the intramolecular vibrations In metallic and fully ionic charge transfer complexes, these intramolecular vibrations are the vibrations of anions [36] but in the present cases of semiconducting charge transfer complexes, these bands correspond to the molecular vibrations of donor molecules [37] The spectra are governed by donor vibrations in the charge transfer complexes without dative bindings

The last (sixth) range is below 1300 cm^{-1} which contains one more electronic absorption envelope but with long tailing at longer wavelengths down to those corresponding to 400 cm^{-1} of wavenumbers. The background absorption below 1000 cm^{-1} can be analyzed as an absorption function corresponding to the nature of transition across a low energy band gap This band gap exists in the ternary systems below the low-energy envelope.

The ternary CT complexes thus contain three bands involved in two transitions across the gaps two conduction band and one valence band [38] Within the Peierls gap, one more band corresponding to an anionic sublattice penetrates the gap making one more band-to-band transition possible with much lesser band gap These two electronic transitions are analyzed here (Figures 2 (a-d) and Figures 3(a-d) The high energy transition is found to be usually a direct transition except in benzidine-TCNE-I_2 as in the cases of binary purely organic charge transfer complexes The low energy transition in all cases are found to be an indirect transition, i e involving absorption and reemission of a phonon This shows that the sublattice of organic radical anion provides an associated band edge [28] which is shifted in momentum or wavenumber in the band structure associated with a binary complex The details of two transitions are summarized (Table 1)

The data analysis in third range, *i e* between 2200 cm^{-1} and 3000 cm^{-1} by plotting $\ln\alpha$ *vs* $h\nu$ reveals exponentially decaying band edge above the transition range $(h\nu > E_g)$ The width of the band tail is described by [39]

$$\alpha = \alpha_0 \exp\left((h\upsilon - E_1)/E_0\right)$$

and is explicitly given by

$$E_0 = \left(\partial \ln \alpha / \partial\, h\upsilon\right)^{-1}$$

Table 1 Nature of transitions at higher and lower infrared absorption edges in ternary systems

Name of ternary complex	Absorption function in 0 2-0 3 eV range	Nature of transition and value of E_g (eV)	Absorption function in 0 05-0 15 eV range	Nature of transition and value of E_g (eV)
Benzidine-chloranil-I_2	$\alpha h\nu = A(h\nu - E_g)^{1/2}$	Forbidden direct (0 22 eV)	$\alpha h\nu = A(h\nu - E_g)^3$	Forbidden direct (0 05 eV)
Benzidine-DDQ-I_2	$\alpha h\nu = A(h\nu - E_g)^{1/2}$	Forbidden direct (0 26 eV)	$\alpha h\nu = A(h\nu - E_g)^2$	Allowed direct (0 05 eV)
Benzidine-TCNQ-I_2	$\alpha h\nu = A(h\nu - E_g)^{1/2}$	Allowed direct (0 26 eV)	$\alpha h\nu = A(h\nu - E_g)^3$	Forbidden direct (0 07 eV)
Benzidine-TCNE-I_2	$\alpha h\nu = A(h\nu - E_g)^3$	Forbidden direct (0 22 eV)	$\alpha h\nu = A(h\nu - E_g)^2$	Allowed direct (0 05 eV)

Table 2 Free carrier absorption and band tailing in ternary systems

Name of ternary complex	Slope of $\log\alpha$ *vs* $\log\lambda$ for $h\nu > E_g$	Scattering mechamism	Reciprocal of the slope of $\log\alpha$ *vs* $\log h\nu$ E_0(eV)	Nature of material and value of E_d/K_BT
Benzidine-chloranil-I_2	2 5	Optical phonon scattering	0 24 eV	Strongly disordered (9 23)
Benzidine-DDQ-I_2	4 2	Ionized impurity scattering	0 18 eV	Disordered (6 29)
Benzidine-TCNQ-I_2	3 3	Ionized impurity scattering	0 20 eV	Diordered (7 69)
Benzidine-TCNE-I_2	4 2	Ionized impurity scattering	0.10 eV	Weakly disordered (3 85)

This analysis is shown in Figures 4(a-d)

It was found that this edge was not modified due to the internal electric field to obey $(\ln \alpha)^{2/3}$ *vs* $h\nu$ as a straight line as suggesting internal Franz-Keldysh effect [40] related with the interband tunneling of charge carriers Thus the local electric field inside are not sufficient to create Zener tunneling. The values of E_0 in the four ternary conductors suggest that the large band tail (E_0=0 24 eV, E_0/K_bT~9) in benzidine-chloranil-I_2 corresponds to the maximum disorder due to weak charge transfer binding in this complex The minimum disorder characterized by low value of band tailing width (E_0=0 10 eV, E_0/

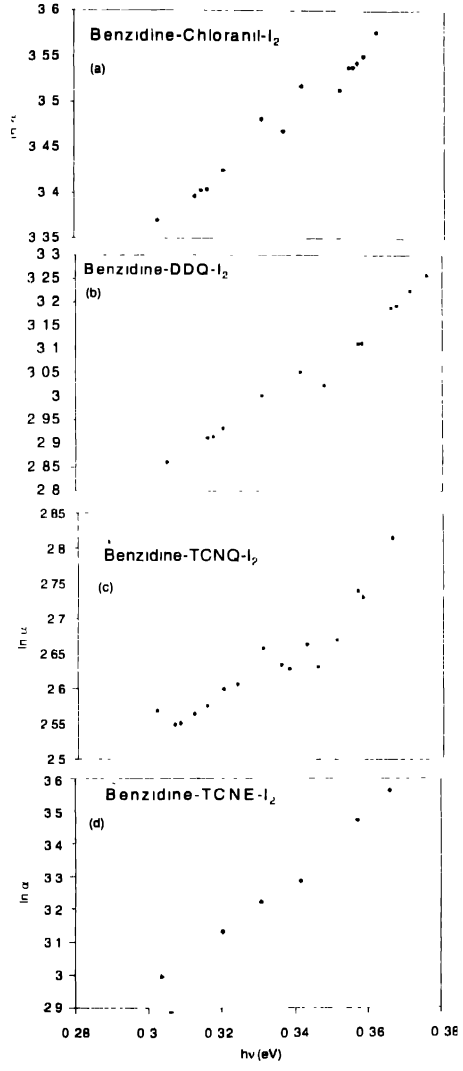

Figure 4. Band tailing analysis by plotting $\ln\alpha$ *vs* $h\nu$ for (a) Benzidine-Chloranil -I_2, (b) Benzidine-DDQ-I_2, (c) Benzidine-TCNQ-I_2 and (d) Benzidine-TCNE-I_2

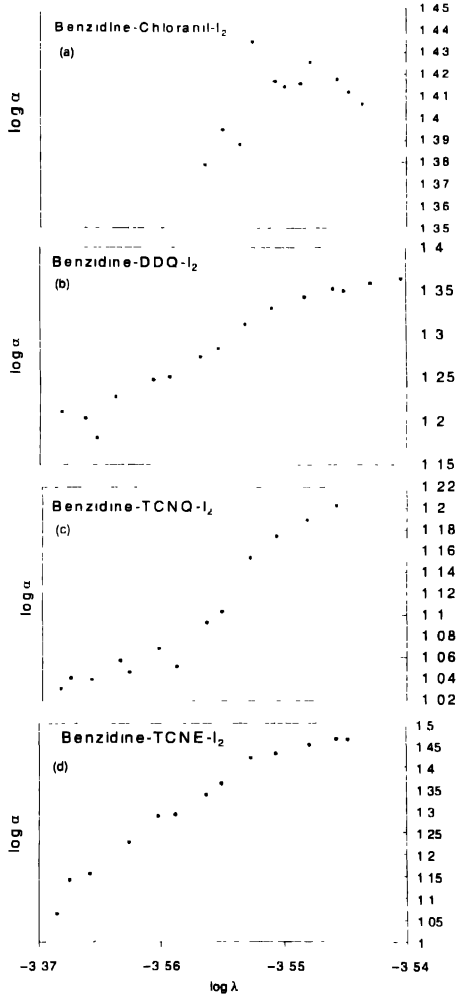

Figure 5. Free carrier absorption (scattering mechanism) analysis by plotting $\log\alpha$ *vs* $\log\lambda$ for (a) Benzidine-Chloranil-I_2; (b) Benzidine-DDQ-I_2, (c) Benzidine-TCNQ-I_2 and (d) Benzidine-TCNE-I_2

K_bT ~3.5) in benzidine-TCNE-I_2 is consistent with strong CT interaction between benzidine and TCNE. This is all summarized in Table 2

The analysis of free carrier absorption in the first range above 3500 cm^{-1} where the absorption coefficient increases with an increase in wavelength according to

$$\alpha_f = A\lambda^{1.5} + B\lambda^{2.5} + C\lambda^{3.5},$$

has been made

Usually, one type of mechanism is dominative [30] The analysis is done by plotting $\log\alpha$ vs $\log\lambda$ (Figures 5(a-d)) The data analysis reveals scattering by optical phonons (slope~2 5) in benzidine-Chloranil-I_2 and scattering by ionized impurities (slope~3 2-4 2) in other three ternary conductors These results are consistent with the disordered nature found with band tailing in ternary compound to binary CT complexes The strong disorder suggests ionized I_3 ions to be situated at the non-specific sites available and therefore, acting as ionized impurities The disorder along iodide sublattice is maximum when CT interactions are weak and disorder is maximum when CT interactions are strong Only in benzidine-chloranil-I_2, there is participation of optical phonons when there is maximum interaction between benzidine and chloranil DDQ forms a semiquinone ion more easily than chloranil due to asymmetry and highly electronegative chlorine ions replaced by cyano groups Chloranil due to highly electronegative chlorine ions contained less negative charges on two oxygen ions and therefore, less prone to formation of semiquinone ion

4. Conclusion

The four ternary CT complexes of benzidine having semiconducting binary subsystems are not strongly disordered compared to binary CTCs Two- band transport mechanism is followed with indirect low – energy transmission due to associated band edge Both band tailing analysis and free carrier absorption analysis both suggests disordered nature and scattering by ionized impurities The materials are degenerate semiconductors rather than semimetals or impure alloys

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